Field Sampling and Analytical Methods for Explosive Compounds

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Outline of Presentation

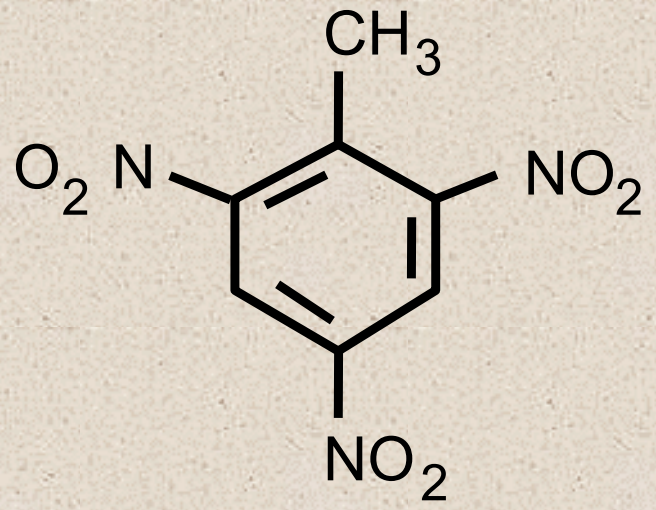
- Important properties of nitroaromatic (TNT) and nitramine (RDX) explosives
- Accepted laboratory methods for explosive chemicals
- Detection criteria for explosives-related chemicals
- Why you should consider using on-site methods
- Sampling considerations for explosives in soil and water
- Verified methods for on-site determination of explosives in soil and water
- Advantages/disadvantages of various on-site methods
- Training range characterization

Safety

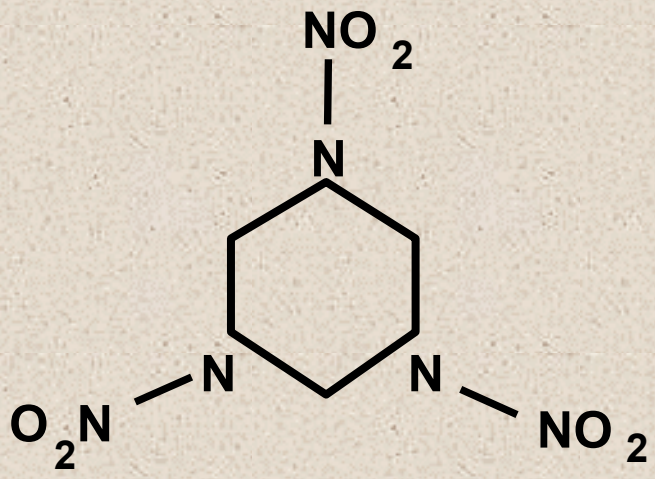
- Chunks of high explosives are often found at contaminated sites.
- Concentrations of TNT or RDX greater than 12% in soil are reactive (can propagate a detonation).*
- Neither chunks nor soil with concentrations of TNT and RDX greater than 10% can be shipped off-site using normal shipping procedures.
- Use on-site methods to screen for high concentrations before shipment.

*Kristoff et al. 1987

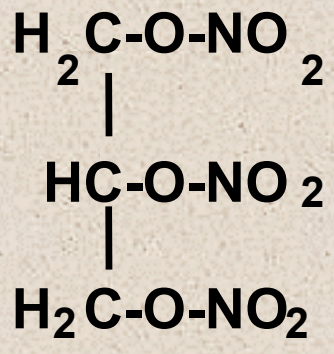
Nitroaromatics
(TNT)



Nitramines
(RDX)



Nitrate Esters
(NG)



Physical and Chemical Properties of Explosive Chemicals

- Most are solids at environmental temperatures.
- Sources often are particulate at soil surface.
- Have low aqueous solubilities.
- Surface contamination persists for long periods (50-100 years).
- Once dissolved, RDX can migrate rapidly through vadose zone.
- TNT readily biotransforms.
- Relatively nonvolatile.
- Thermally labile.

EPA SW-846 – Standard Laboratory Methods for Nitroaromatic and Nitramine Explosives in Soil and Water

- Sample preparation

  Water: Salting-out or solid-phase extraction

  Soil: Ultrasonic extraction with acetonitrile

- Determination

  SW-846 Method 8330 (RP-HPLC-UV)

  SW-846 Method 8095 (GC-ECD) (draft)

- www.epa.gov/epaoswer/hazwaste/test/index.htm

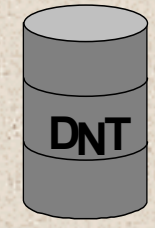
Current Detection Capabilities for Soil Analysis (MDL)

	SW-846 Method 8330 RP-HPLC-UV	SW-846 Method 8095 GC-ECD
TNT	32 µg/kg	2 µg/kg
RDX	68 µg/kg	6 µg/kg
HMX	52 µg/kg	10 µg/kg
NG	40 µg/kg	10 µg/kg

Soil Sampling Strategy for Nature and Extent of Contamination

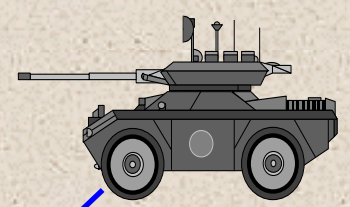
- Traditional approach uses large sampling grids, small number of discrete samples, and off-site analysis.
- Initial sampling studies characterized degree of spatial heterogeneity
  - Compared sampling error to analytical error
  - Investigated use of composite samples to improve representativeness
  - Compared results from on-site and laboratory analyses

Locations for Initial Sampling Studies



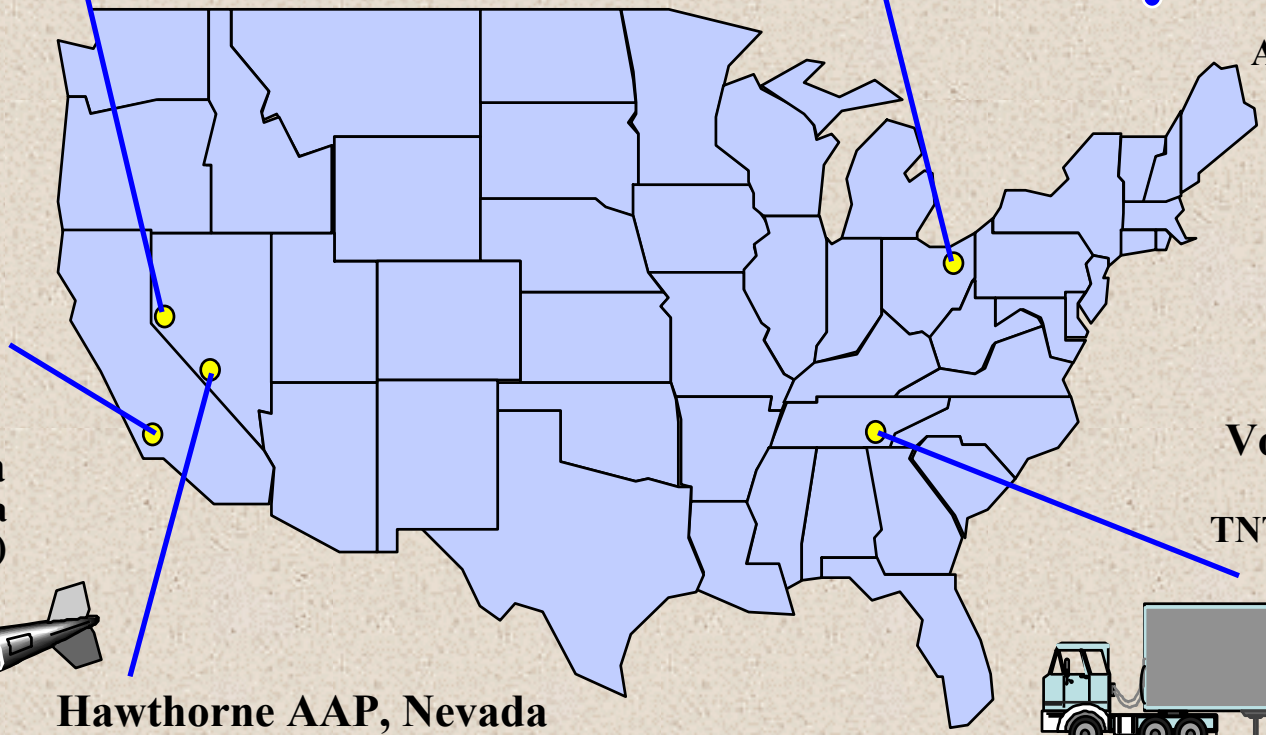
BLM Sparks
Reno, Nevada (Monite)
Abandoned Industrial Site
Administered by BLM

Ravenna AAP, Ohio
Load, Assemble, and Pack Facility



CFB
Valcartier
Anti-Tank Range

Fort Ord,
California
Impact Area
(BRAC Site)



Hawthorne AAP, Nevada
Load, Assemble, and Pack Facility
(Army, Navy)

Volunteer AAP
Tennessee
TNT Manufacturing
Installation

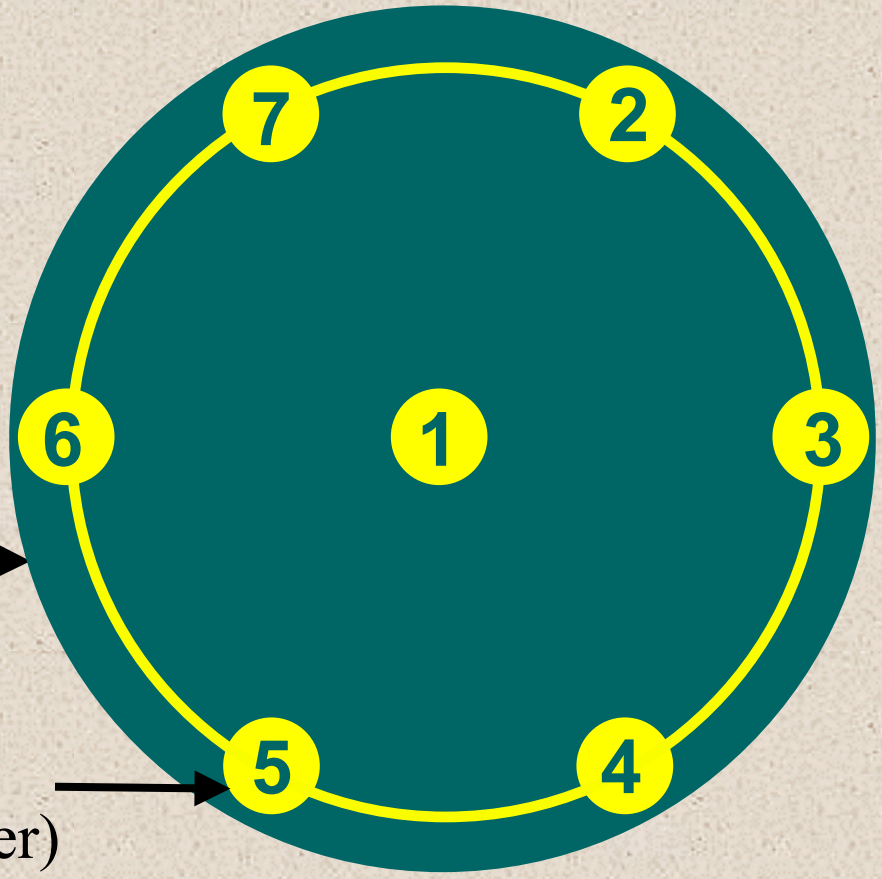
Field Sampling Scheme

Samples arranged in a wheel pattern

Surface samples 0 cm to 15 cm

Diameter of wheel = 122 cm

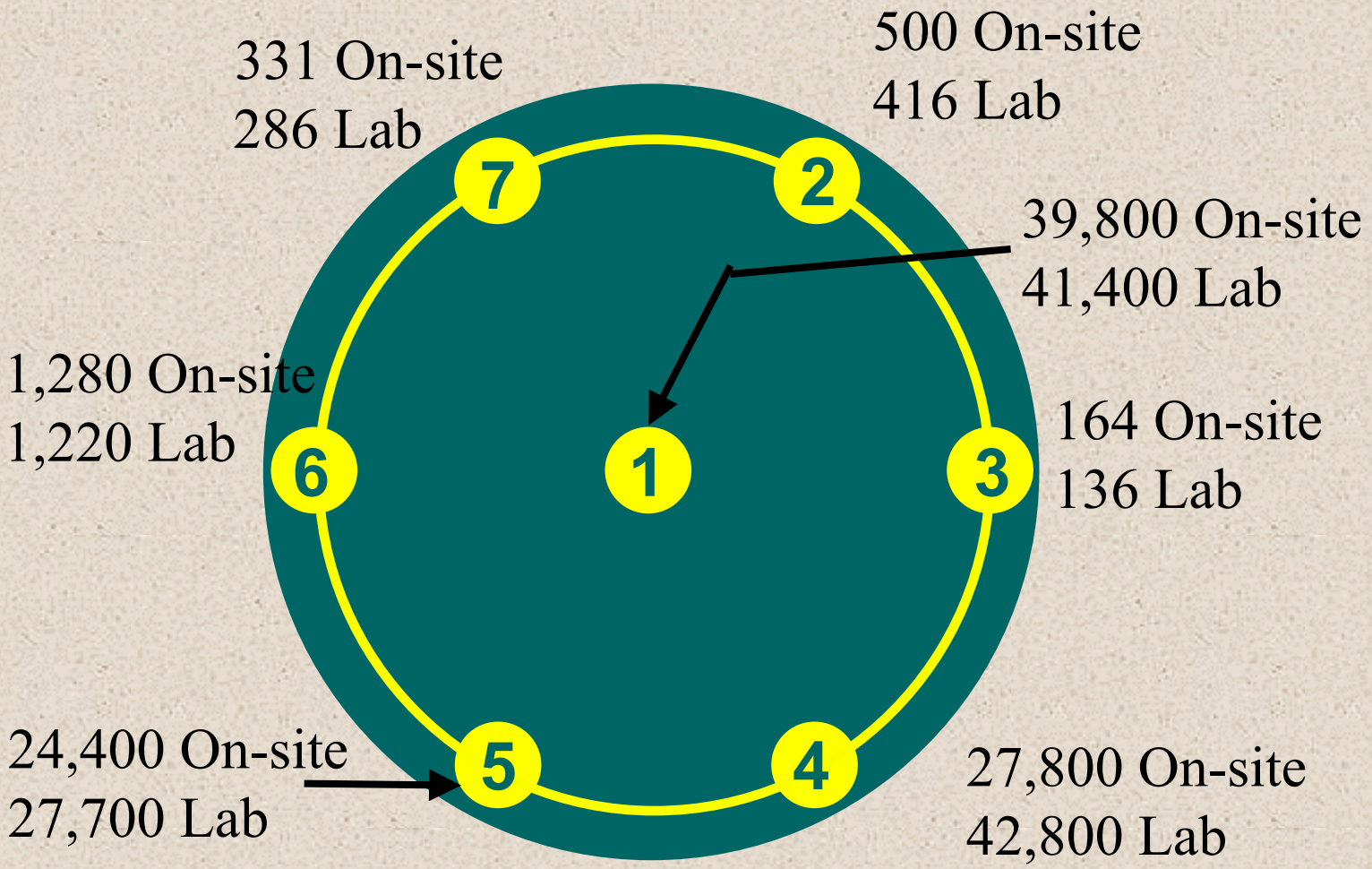
Diameter of sampler = 5 cm (stainless steel auger)



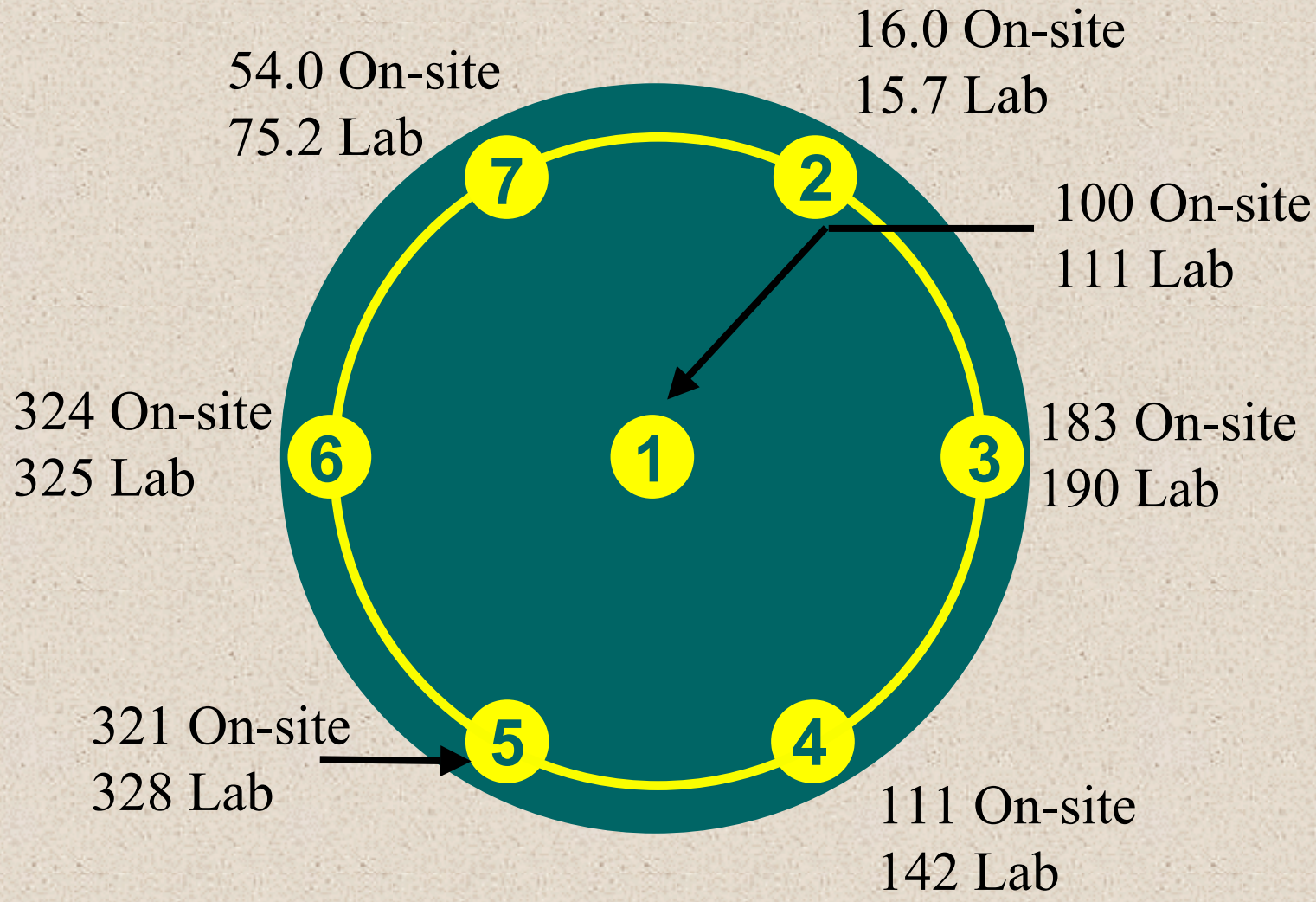

C1
C2
C3
C4
C5
C6
C7
Composites
1A
1B
2A
2B
3A
3B
4A
4B
5A
5B
6A
6B
7A
7B
INDIVIDUALS
SITE 1


JACKPOT PORTER
BREWMASTER'S SEASONAL SPECIALS

Monite Site, Sampling Location #1 Major Analyte: TNT (mg/kg)



Valcartier ATR, Sampling Location #10
Major Analyte: HMX (mg/kg)



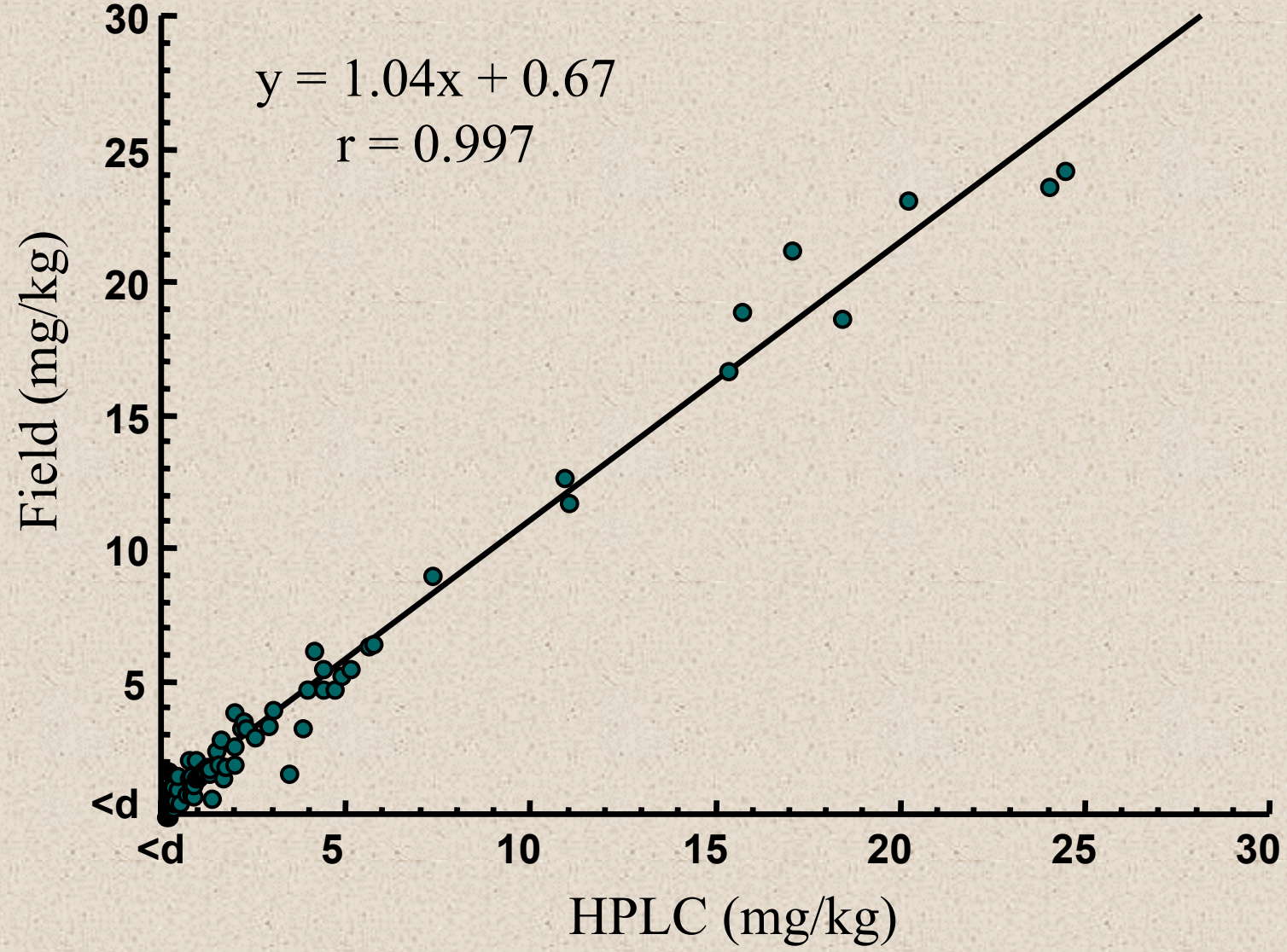
Data Analysis from Sampling Studies

- Analytical error for each type estimated by reproducibility of duplicate on-site and laboratory analyses
- Sampling error estimated by differences in mean values between sampling locations
- Accuracy of on-site methods estimated by comparison of mean values between on-site and laboratory analyses

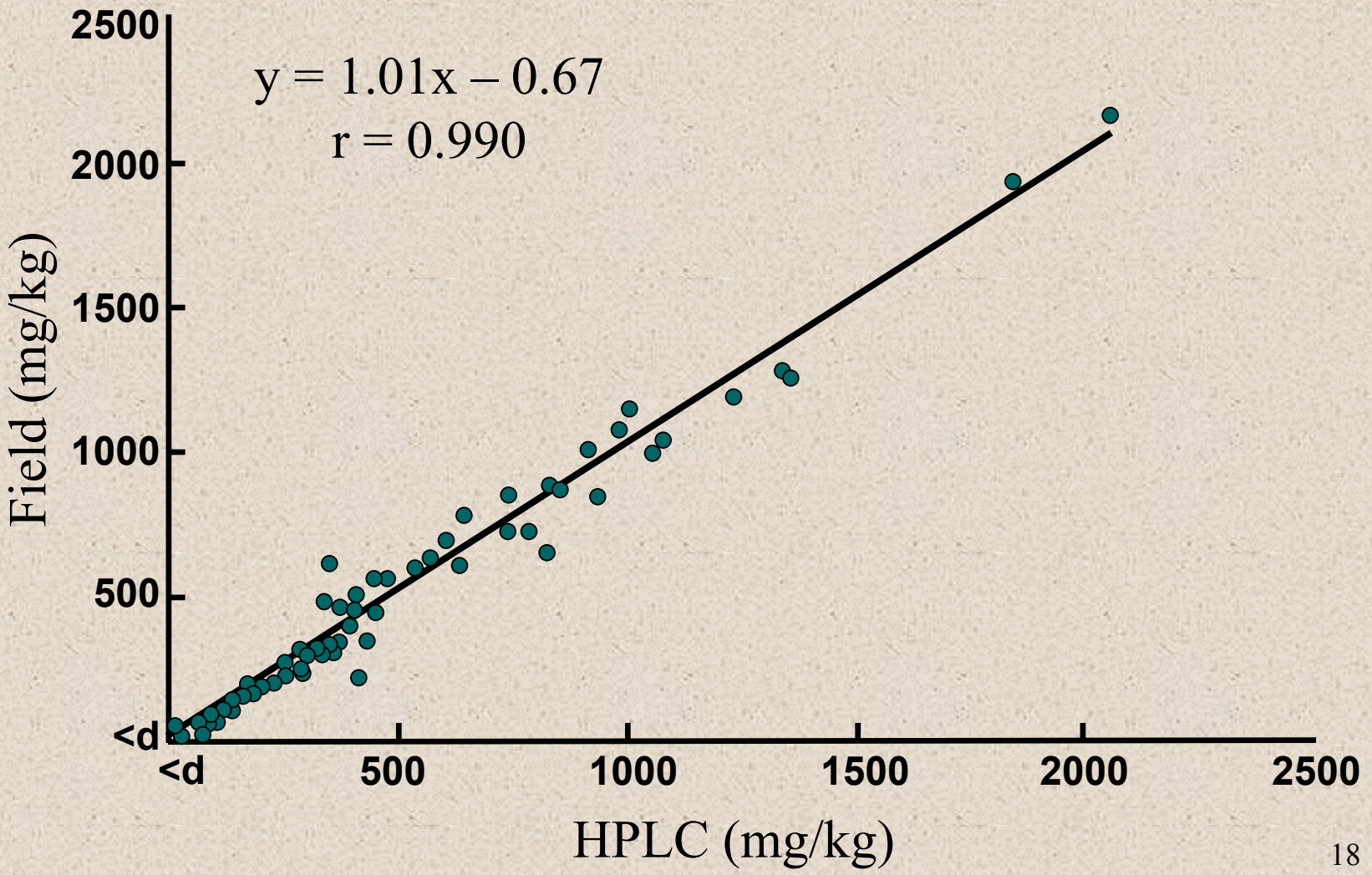
Soil Analyses: On-Site and Laboratory Methods
Monite Site and Hawthorne AAP

			Discrete Samples			Composite Samples		
Sampling Location	Major Analyte	Field or Lab	Mean	±	SD	Mean	±	SD
Monite, location 1	TNT	F L	13500 16300	± ±	16800 20200	13100 14100	± ±	532 1420
Monite, location 2	DNT	F L	16100 34800	± ±	11700 42200	23800 33600	± ±	3140 2390
Monite, location 3	TNT	F L	19.8 12.9	± ±	42.0 29.0	12.6 4.16	± ±	1.2 0.7
Hawthorne, location 4	TNT	F L	1970 2160	± ±	1980 2160	1750 2000	± ±	178 298
Hawthorne, location 5	TNT	F L	156 168	± ±	121 131	139 193	± ±	16.6 7.7
Hawthorne, location 6	Ammonium Picrate	F L	869 901	± ±	1600 1660	970 1010	± ±	32 92

CFB-Valcartier: TNT Concentrations On-Site vs. Laboratory Results



CFB-Valcartier: HMX Concentrations On-Site vs. Laboratory Results



Sampling Experiment at Ft. Polk Artillery Range Impact Area

- Experiment conducted within a 10-m x 10-m sampling grid
- Samples collected in one-hundred 1-m x 1-m minigrids
- Grid contaminated with residues from a low-order (partial) detonation of an 81-mm mortar
- Samples collected in top 2.5 cm of soil

RDX Concentrations (µg/g) in a 10-m X 10-m Area at an Artillery/Mortar Impact Area

17.1	1.27	0.829	0.908	10.9	4.44	0.437	0.354	1.52	0.067
0.805	24.1	7.73	0.539	0.260	0.233	0.366	1.93	0.731	0.138
30.8	1.40	12.5	0.342	0.074	1.11	0.18	0.076	7.11	0.187
12.7	138	53.7	3.85	4.94	1.22	4.63	0.470	2.41	1.06
331	9.70	3.96	1.44	3.67	0.243	3.21	0.254	1.03	0.073
7.52	5.65	1.97	0.571	4.84	19.9	0.825	0.122	1.46	0.070
1.65	1.56	8.51	10.6	2.24	25.2	7.15	0.248	0.175	0.037
48.3	13.3	3.36	6.93	889	21.8	3.75	0.618	0.193	0.081
1.18	1.03	64.3	557	1790	2390	11.3	1.65	0.335	0.263
8.86	3.50	5.02	42.7	385	24.9	3.64	0.96	0.526	0.161

10-m

Results from Ft. Polk Sampling Experiment

- Sampling grid contained small chunks of undetonated explosive (total mass 198-g)
- RDX concentrations in discrete surface soil samples ranged over 5 orders of magnitude (0.04 to 2390 mg/kg)
- RDX concentrations in ten 25-increment composite soil samples ranged from 4.6 to 294 mg/kg

Soil Sampling Considerations for Explosives-Contaminated Sites

- Concentrations in soil are spatially very heterogeneous over very short distances.
- For discrete samples, sampling error >> analytical error.
- Composite samples provide more representative data than discrete samples.
- Research to optimize sampling protocols for various types of ranges is underway

- Subsampling error – effect of grinding on standard deviation in hand grenade range soil


Soil prior to grinding.

Subsample	TNT Conc. mg/kg		RDX Conc. mg/kg	
	Not Ground	Ground	Not Ground	Ground
1	0.25	2.03	1.68	4.75
2	1.81	2.04	1.77	4.71
3	0.37	2.00	1.46	4.80
4	1.48	2.03	3.80	4.73
5	7.93	1.97	7.83	4.67
6	0.56	2.00	1.81	4.66
7	0.35	1.90	2.35	4.62
8	0.75	2.02	2.51	4.62
9	0.56	1.97	2.08	4.64
10	0.35	1.98	1.98	4.69
11	0.62	1.90	1.68	4.66
12	5.62	1.91	13.0	4.60
mean	1.72	1.98	3.50	4.68
std dev	2.46	0.051	3.47	0.057
RSD	143%	2.57%	99%	1.23%

Frequency of Occurrence of Explosives Analytes in Laboratory Analyses

- Soil samples (explosives detected: 28%)
  - Contaminated samples
    TNT: 66%
    RDX: 27%
    TNT, RDX, or 2,4-DNT: 94%
- Water samples (explosives detected: 14%)
  - Contaminated samples
    TNT: 56%
    RDX: 61%
    TNT or RDX: 94%

Source: Walsh et al. 1993

Recommended On-Site Technologies for Explosives

- EXPRAY Kit (Plexus Scientific)
- EnSys Colorimetric TNT and RDX/HMX Kits (SDI)
- DTECH Enzyme Immunoassay Kits (SDI)
- GC-TID (SRI Instruments)

EXPRAY Kit

- Simplest screening kit (colorimetric)
- Useful for surfaces and unknown solids
- Can be used to provide qualitative test for soils
- Kit contains three spray cans

  EXPRAY 1 - Nitroaromatics (TNT)

  EXPRAY 2 - Nitramines (RDX) and nitrate esters (NG)

  EXPRAY 3 - Black powder, ANFO

- Spray cans used sequentially


double-tipped cotton swabs

Use of EXPRAY Kit

- For surfaces or unknown solid
  1. Wipe surface with sticky collection paper
  2. Spray paper with EXPRAY
- For soil
  1. Place soil on top of two filter papers
  2. Soak soil with acetone
  3. Spray the bottom filter paper with EXPRAY reagents (spray cans used sequentially)
- Detection limit – 20 ng

EXPRAY for Unknown Solids

EXPRAY Kit

- Available from:

  Plexus Scientific
  12501 Prosperity Drive, Suite 401
  Silver Spring, MD 20904

  Phone: (301) 622-9696
  Fax: (301) 622-9693

- Cost is $400/kit
- Even if other technologies are being used, the EXPRAY kit should be available

EnSys Colorimetric Test Kits
EPA SW-846 Methods 8515 and 8510

- Initial TNT method developed by CRREL 1990* (8515)
- Initial RDX method developed by CRREL 1991** (8510)
- Commercialized by EnSys, now SDI
- Colorimetric methods for TNT and RDX/HMX
- Successfully used at variety of explosives sites
- Results correlate well with Method 8330
- TNT kits cost $410 for 20 tests ($20.50/sample)
- RDX kits cost $500 for 20 tests ($25/sample)

* Jenkins 1990 **Walsh and Jenkins 1991

Characteristics of Colorimetric Kits

- TNT and RDX/HMX tests produce reddish-colored solutions.
- Concentrations are proportional to intensity of color measured with a field portable spectophotometer.
- TNT test also responds to 2,4-DNT, tetryl, TNB.
- RDX/HMX test also responds to NG, PETN, NC, tetryl.
- TNT test is subject to interference from yellow color produced from reaction with humic substances and molecular sulfur (EnSys only).
- RDX/HMX test is subject to interference from nitrate ion unless the optional ion exchange step is used.

Advantages/Disadvantages of Colorimetric Methods

Advantages

- Easy to use in the field
- Good quantitative agreement with laboratory results
- Dilutions do not require use of an additional kit
- Screens for presence of nontargeted explosives
- Successfully used at many contaminated sites
- Good method to assess reactivity of soil prior to shipping

Disadvantages

- Requires some experience with chemical analysis
- Class-specific but not analyte-specific
- Yellow color from humics can interfere with TNT test
- Use for water samples requires preconcentration (SPE)

EnSys Colorimetric TNT and RDX/HMX Kits

- Kits available from:

  Strategic Diagnostics Inc. (SDI)
  128 Sandy Drive
  Newark, DE 19713-1147

  Phone: (302) 456-6789
  Fax: (302) 456-6770

- Spectrophotometer available from:

  Hach Company
  P.O. Box 608
  Loveland, CO 80539-0608

  Phone: (800) 227-4224
  Fax: (970) 669-2932

DTECH Enzyme Immunoassay Test Kits EPA SW-846 Methods 4050 and 4051

- TNT method developed by SDI 1993*
- RDX method developed by SDI 1994**
- Immunoassay methods for TNT and RDX
- More selective than colorimetric, but some cross-reactivity
- Successfully used at variety of sites
- Results given in concentration range; ranges in general agreement with results from Method 8330
- TNT kits cost $130 for 4 tests ($32.50/sample)
- RDX kits cost $130 for 4 tests ($32.50/sample)

* Hutter et al. 1993 ** Teaney and Hudak 1994

Advantages/Disadvantages of DTECH Immunoassay Methods

Advantages

- Configured for ease of use in the field
- Requires less training/experience
- Relatively specific for TNT and RDX
- Successfully used at many contaminated sites
- No preconcentration required for water analysis

Disadvantages

- Fair quantitative agreement with laboratory results
- Provides only concentration range
- Provides no information on nontarget analytes
- Additional kit required for dilutions

DTECH Immunoassay TNT and RDX Kits

- Available from:

  Strategic Diagnostics Inc. (SDI)
  128 Sandy Drive
  Newark, DE 19713-1147
  Phone: (302) 456-6789
  Fax: (302) 456-6770

Environmental Technology Verification (ETV)

- Conducted by Oak Ridge NL for EPA/DoD
- 108 blind soil samples and 176 blind water samples
- Results compared to SW-846 Method 8330
- 1999 demonstration (results on website)*
  - Research International/NRL Fast 2000
  - Barringer GC-Ionscan
- 2000 demonstration (results on website)*
  - SRI/CRREL GC-Thermionic
  - Texas Instruments SPREETA

*http://www.epa.gov/etv

SRI/CRREL GC-TID Method

- GC-TID instrument manufactured by SRI (Model 8610C)
- Method developed by Hewitt et al. 1999 (CRREL)
- Allows on-site determination of important military high explosives and degradation products and some primary explosives
  - Nitroaromatics: TNT, 2,4-DNT
  - Nitramines: RDX, HMX
  - Nitrate esters: PETN, NG
  - Degradation products: TNB, 2-ADNT, 4-ADNT
- Instrument costs about $10,000

SRI/CRREL GC-TID ETV Results (soil)

	TNT	RDX
Precision (%RSD)	17%	13%
Accuracy (mean recovery)	97%	91%
False positives	1%	0%
False negatives	3%	1%
Completeness	100%	100%
Throughput	3 samples/hr	

Advantages/Disadvantages of SRI/CRREL GC-TID

Advantages

- Provides on-site results for all major target analytes
- Excellent quantitative agreement with laboratory
- Low false positive and false negative rates
- Instrument costs only about $10,000

Disadvantages

- Requires on-site chemist with GC experience
- Requires compressed gases on site
- New method; no track record at real sites

SRI/CRREL GC-TID Method

- Instrument available from:

  SRI Instruments
  20720 Earl Street
  Torrance, CA 90503

  Phone: (310) 214-5092
  Fax: (310) 214-5097

- Methods available from:

  Alan Hewitt
  USA ERDC-CRREL-ESB
  Hanover, NH 03755

  Phone: (603) 646-4388

Why Don't On-Site Analyses and Laboratory Analyses Give Identical Results?

- Heterogeneous distribution of particulate explosives even in properly sampled soil
- Very difficult to split (subsample) moist soils
- Thus, subsamples analyzed on site and those analyzed at an off-site laboratory usually have different analyte contents
- Unfortunately, nonidentical results inaccurately attributed to poor performance of on-site methods
- Unrealistic expectations for level of agreement

Action Criteria for Soils

- No universal criteria established
- Action levels negotiated on a site-specific basis
- EPA Region 3 screening levels (residential)

TNT: 21 mg/kg RDX: 5.8 mg/kg

What About On-Site Methods for Other Explosives?

- Ammonium picrate/picric acid
  - Thorne and Jenkins 1997
- NG and PETN
  - EnSys (SDI) RDX test works for these too
  - SRI/CRREL GC-TID
- Perchlorate
  - Thorne 2004

Recommended Approach To Characterize Explosives - Contaminated Sites

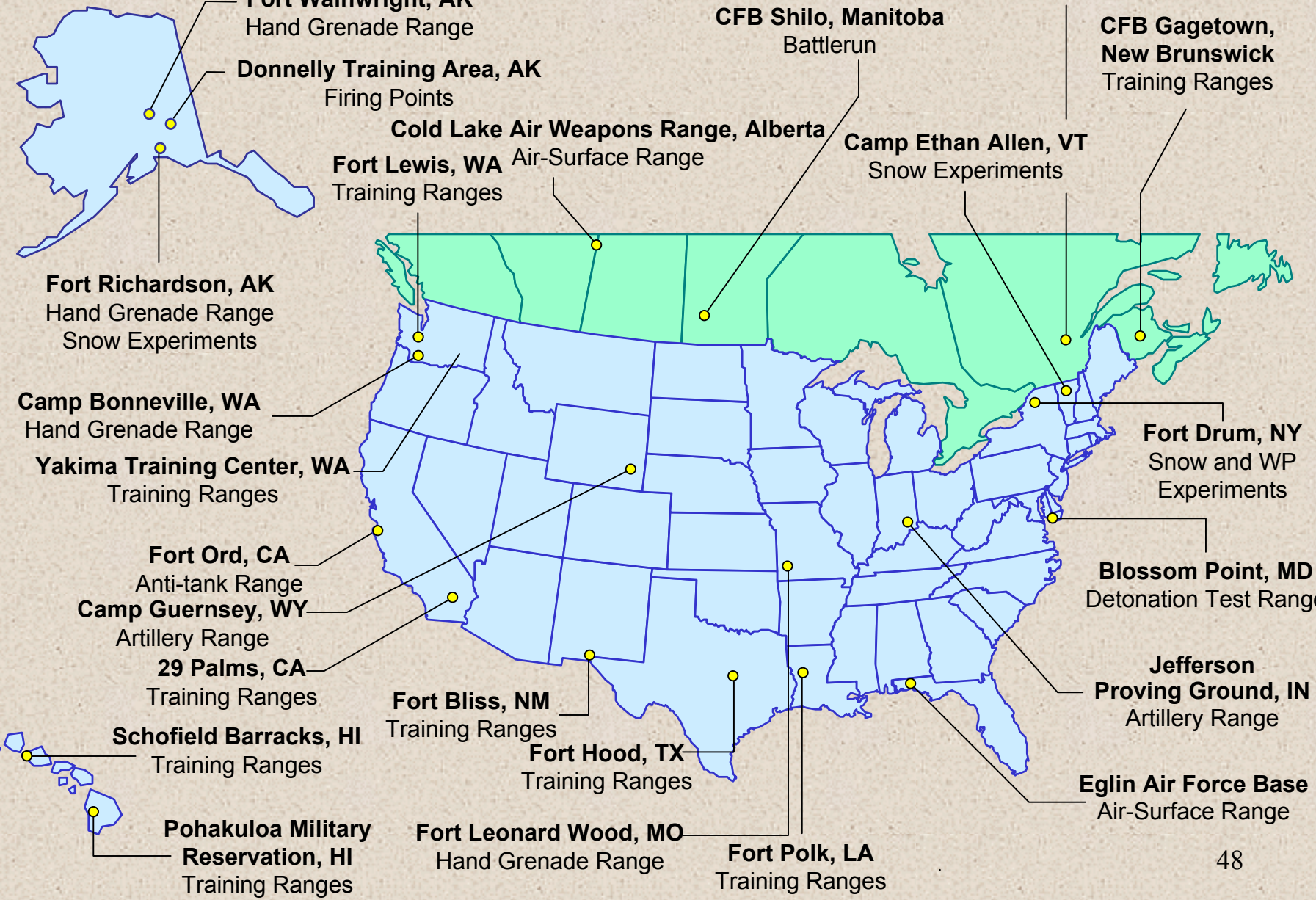
- Conduct small-scale preliminary study
- Use composite sampling with replication to improve representativeness
- Use dynamic work plans and on-site analyses to optimize characterization process (TRIAD)
- SW-846 and ETV have provided information useful for selecting the technology for various applications
- Specify in contract proper subsampling, on-site and lab
- Devote QA attention to sampling and subsampling activities
- Use validated on-site and laboratory methods

Training Range Characterization Research

OBJECTIVES

- To determine best soil sampling strategy to collect representative samples
- To determine on-site and laboratory methods suited to soils from training ranges (explosives)
- To determine the types and distribution of residues at various types of training ranges

Ranges Studied



Surface Soil Sampling

- Analytes heterogeneously distributed
- Multi-increment composite samples necessary to obtain representative samples
- Ranges differ in major analytes present, concentrations, degree of heterogeneity

On-Site and Laboratory Methods for Soils from Ranges

Laboratory Methods

- Detection limits for Method 8330 can be inadequate for low concentrations
- We use Method 8095 for low conc. samples

On-site Methods

- Detection limits for Colorimetric and Immunoassay are about 1 mg/kg
- GC-TID method provides lower detection limits

Sources of Residues of Explosives and Propellants on Training Ranges

- Incomplete propellant combustion during firing activities
- Ordnance blast residues from high-order detonations
- Low-order detonations of various ordnance items
- UXO blow-in-place operations (BIPs)
- Open burning of excess propellant
- Corrosion of surface and subsurface UXO
- Rupture of UXO items by detonations

Difficulties in Estimating Residues from Detonations of Army Munitions

- Testing and training ranges are often contaminated from past operations
- Actual area of deposition on soil is difficult to identify
- Deposition is spatially heterogeneous
- Good estimate of residue deposition requires sampling of large surface areas
- Exact impact area for fired rounds is unpredictable

Advantages of Conducting Residue Studies on Snow-Covered Range

- Fresh snow surface is free of contamination from past detonations
- Easy to differentiate between fresh impacts vs. older ones for fired rounds
- Area of deposition is easy to identify visually
- Large surface area samples are easy to collect

High Tech Sample Collection

M67 Hand Grenade Information

- High explosive – Composition B
- Composition B – 60% RDX, 39% TNT
- Mass of explosives in M67 grenade

RDX – 111 g

TNT – 72 g

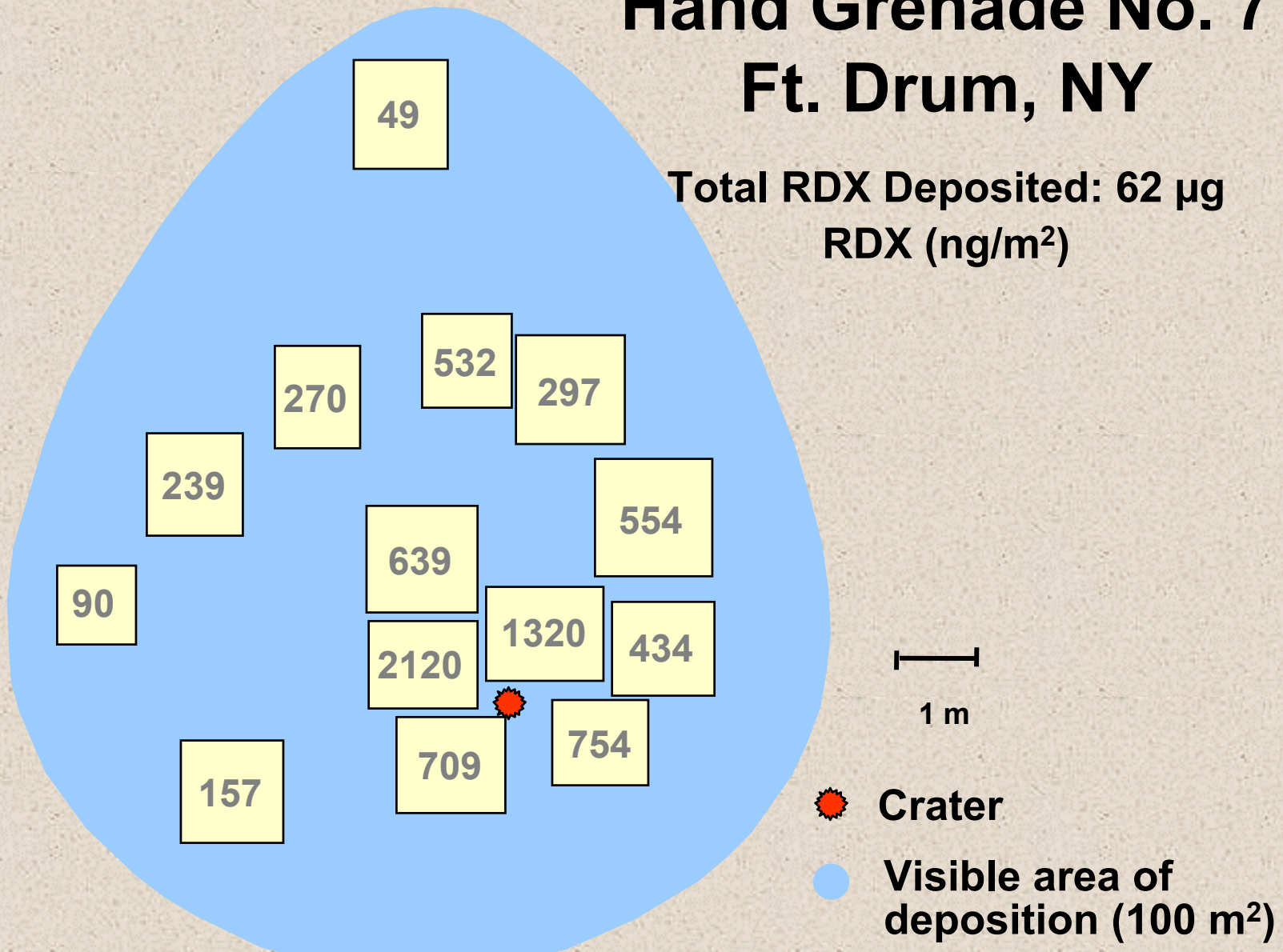
Residues on Snow Surface after Hand Grenade Detonations

Sample Collection
After Hand Grenade Detonations

Hand Grenade No. 7
Ft. Drum, NY

Total RDX Deposited: 62 µg

RDX (ng/m²)



Hand Grenade Residues

Trial #	Area (m^2)	Mass (µg) RDX
1	24	24.1
2	28	20.1
3	25	15.1
4	20	12.8
5	24	16.3
6	30	33.3
7	100	61.8
Mean	36	26.2

Characterization of Explosives Residues at Ft. Lewis Hand Grenade Range

Hand Grenade Low Order Detonations

Estimation of Residue Deposition by Ordnance Item

Munition Type	Residue Deposition (µg)		
	RDX	TNT	HMX
M67 Hand Grenade	26	< 1	< 1
81-mm Mortar (C4)	35,000	240	6,000
C4 Alone	61,000	< 1	26,000
M19 Anti-Tank Mine (C4)	280	< 1	860
M15 Anti-Tank Mine (C4)	4,000	8	410
60-mm Mortar (Point Det.)	630	18	8
60-mm Mortar (Proximity burst)	72	14	19
120-mm Mortar (Point Det.)	4,000	320	140

Hand Grenade Ranges Sampled

- Ft. Lewis, Washington
- Ft. Richardson, Alaska
- WATC-Wainwright, Alberta
- Ft. Leonard Wood, Missouri
- Ft. Wainwright, Alaska
- Camp Bonneville, Washington
- CFB-Gagetown, New Brunswick
- Scholfield Barracks, Hawaii
- Pohakuloa Training Range, Hawaii
- CFB-Valcartier, Quebec

Types of Ranges Characterized

- Hand grenade ranges
- Artillery ranges
- Antitank ranges
- Demolition ranges
- Bombing range
- Firing points

CFB-Valcartier Anti-tank Range

Major Munition Fired
66-mm M72 LAW Rocket

Propellant

- Double-based – nitrocellulose, nitroglycerin

Explosive used in warhead

- Main charge – octol (70%HMX, 30% TNT)
- Booster – RDX

Sampling 10-m X 10-m Grid at Anti-Tank Firing Point

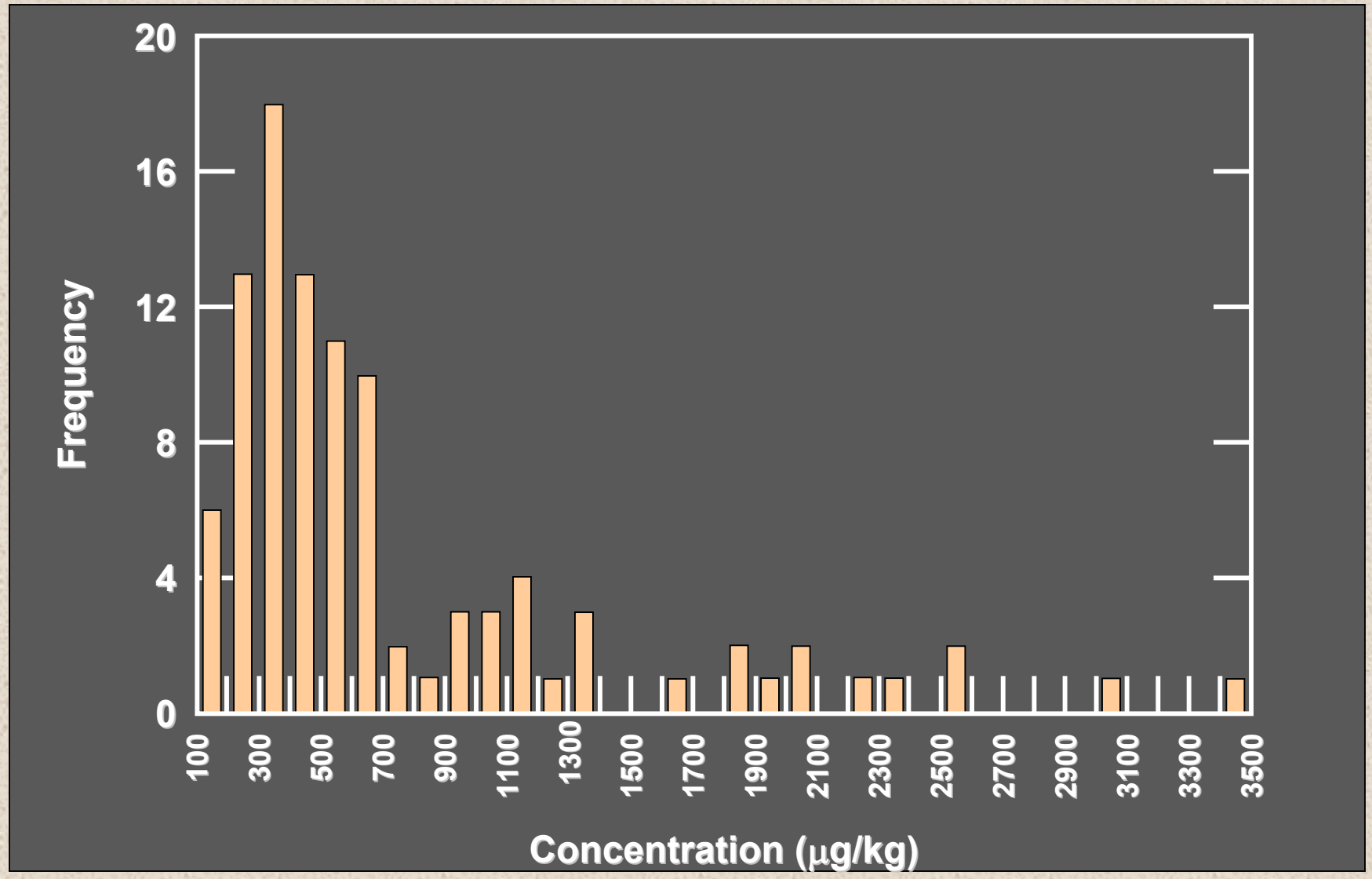
Data Manipulation: Mathematical Composite Samples

- Mathematical composite samples created from random selection of discrete samples:

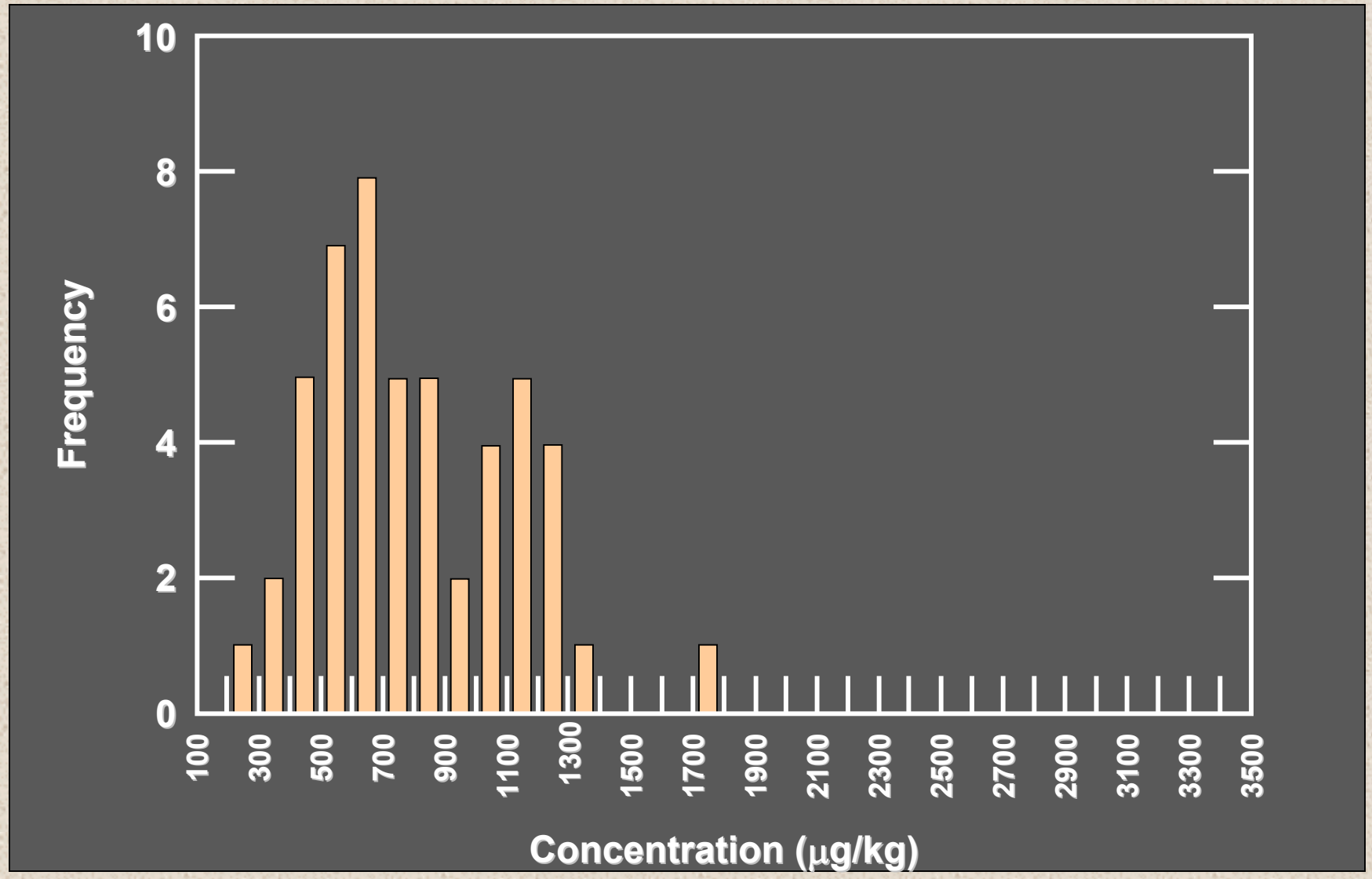
  N = 5, 10, 20, 30, 50

- Obtained 50 tests for each value of N
- Plotted results as histograms (each bin=100) for each value of N (number of increments in composite)

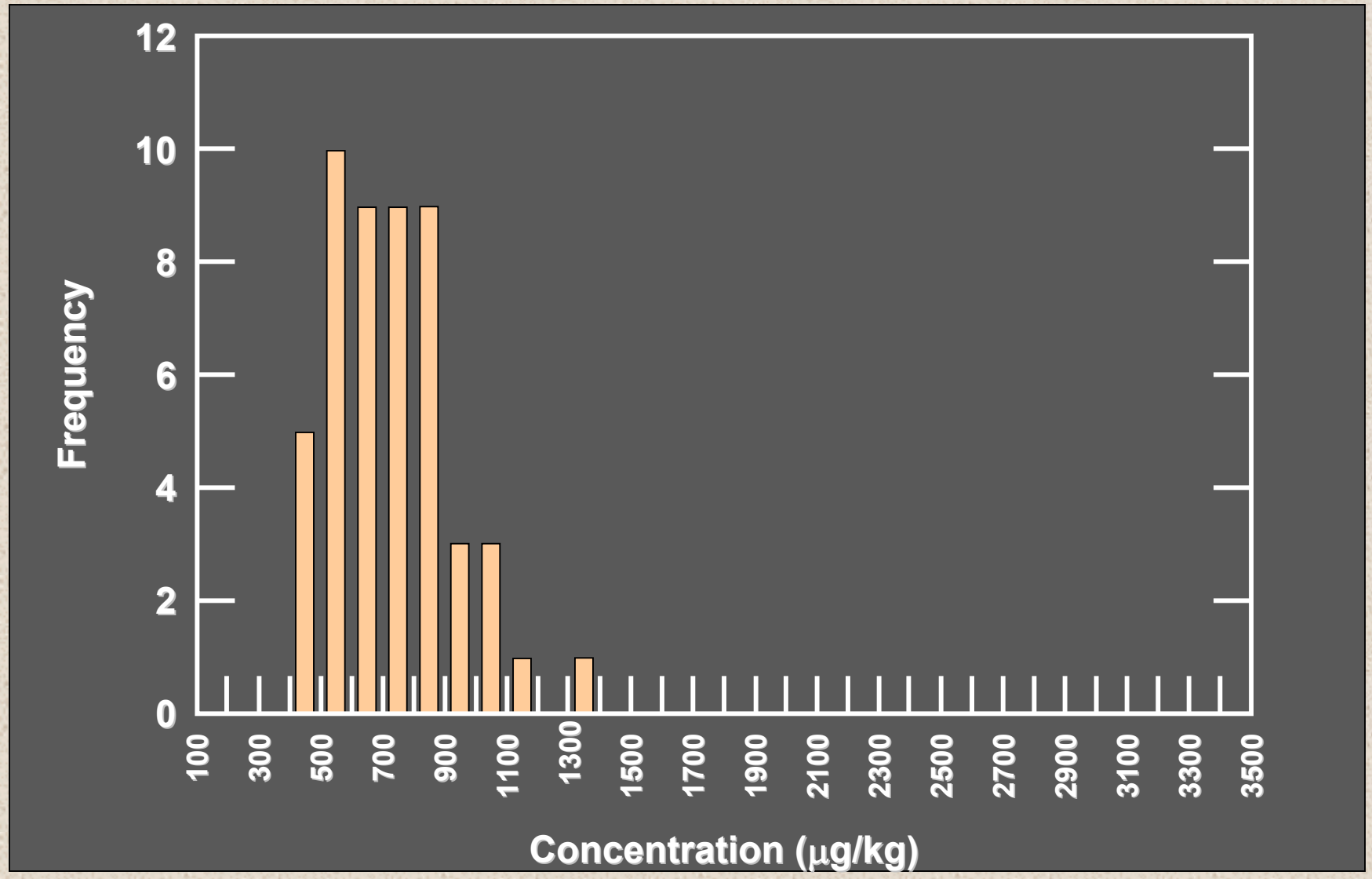
NG Individual Concentrations



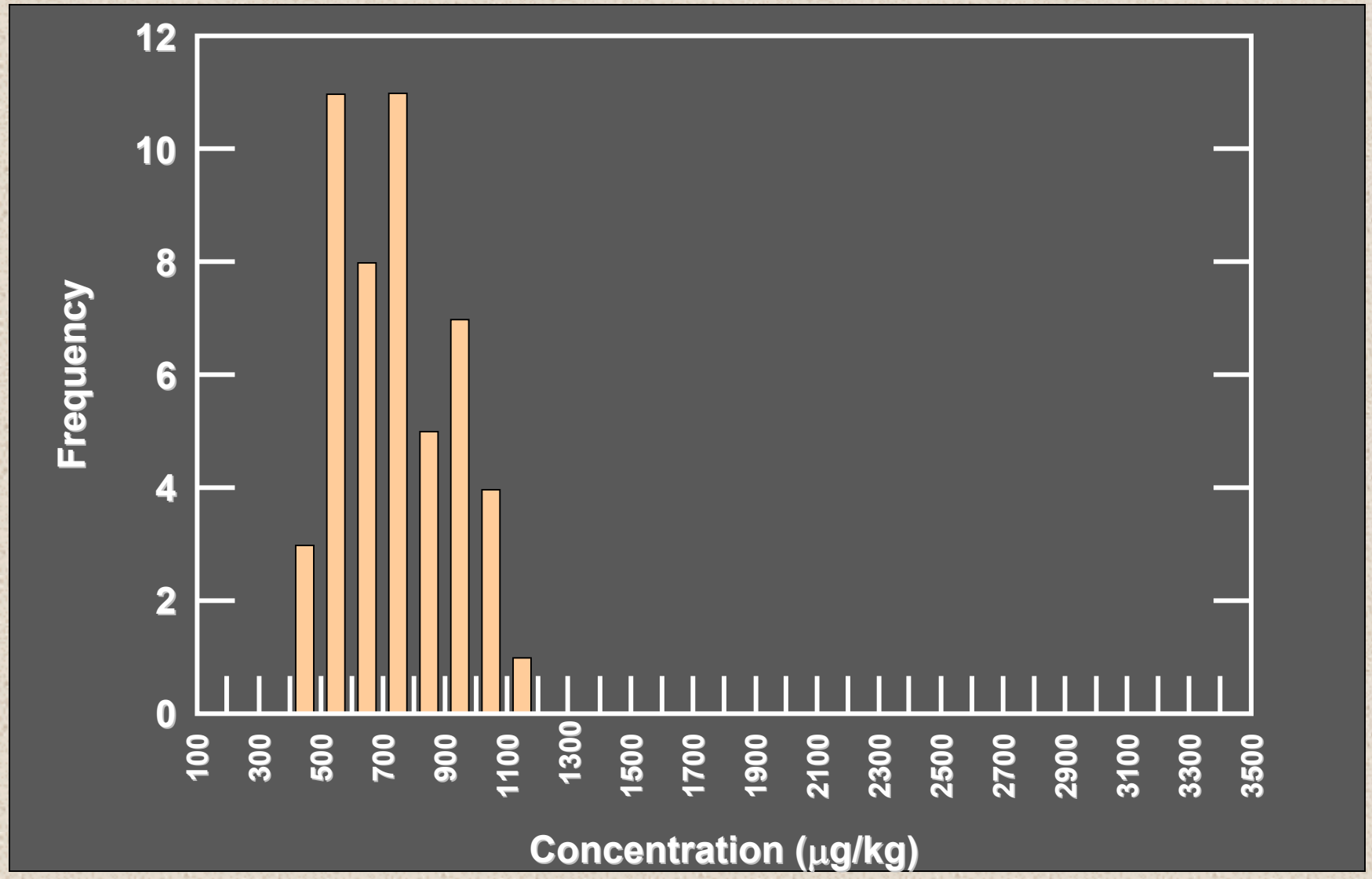
NG Composite (N=5)



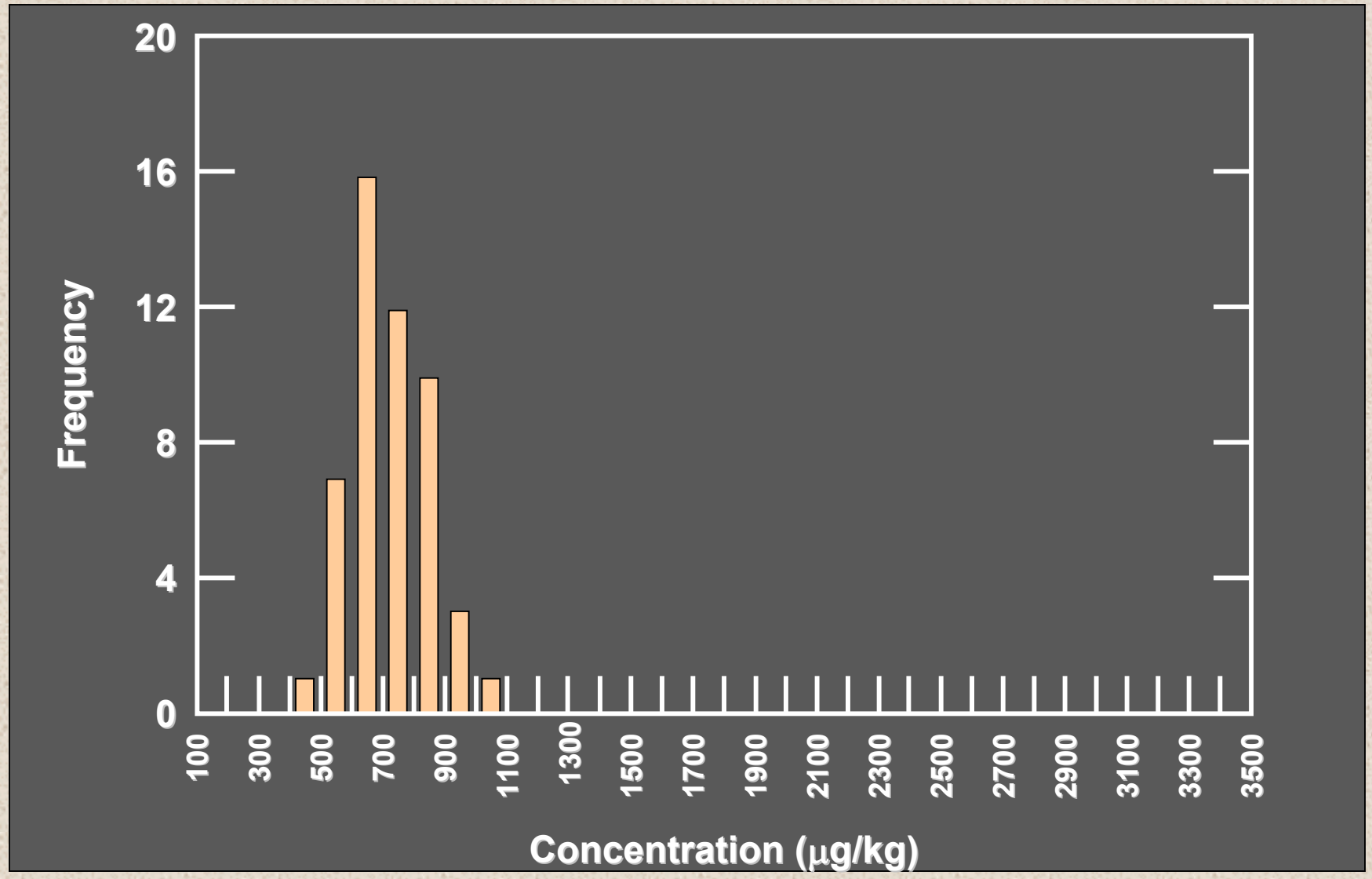
NG Composite (N=10)



NG Composite (N=20)



NG Composite (N=30)



Tolerance Limits for Composite Samples with Various Values of N (NG at Firing Point 10-m X 10-m Grid)

N	Mean	Std Dev.	Tolerance Range(95%)
5	703	316	-185 to 1580
10	628	200	176 to 1080
20	636	182	255 to 1017
30	628	125	372 to 884
40	674	112	447 to 901
50	620	105	409 to 831

Ruptured LAW Rocket and Low-Order 500 lb Bomb

Low-Order 155 mm Howitzer Round

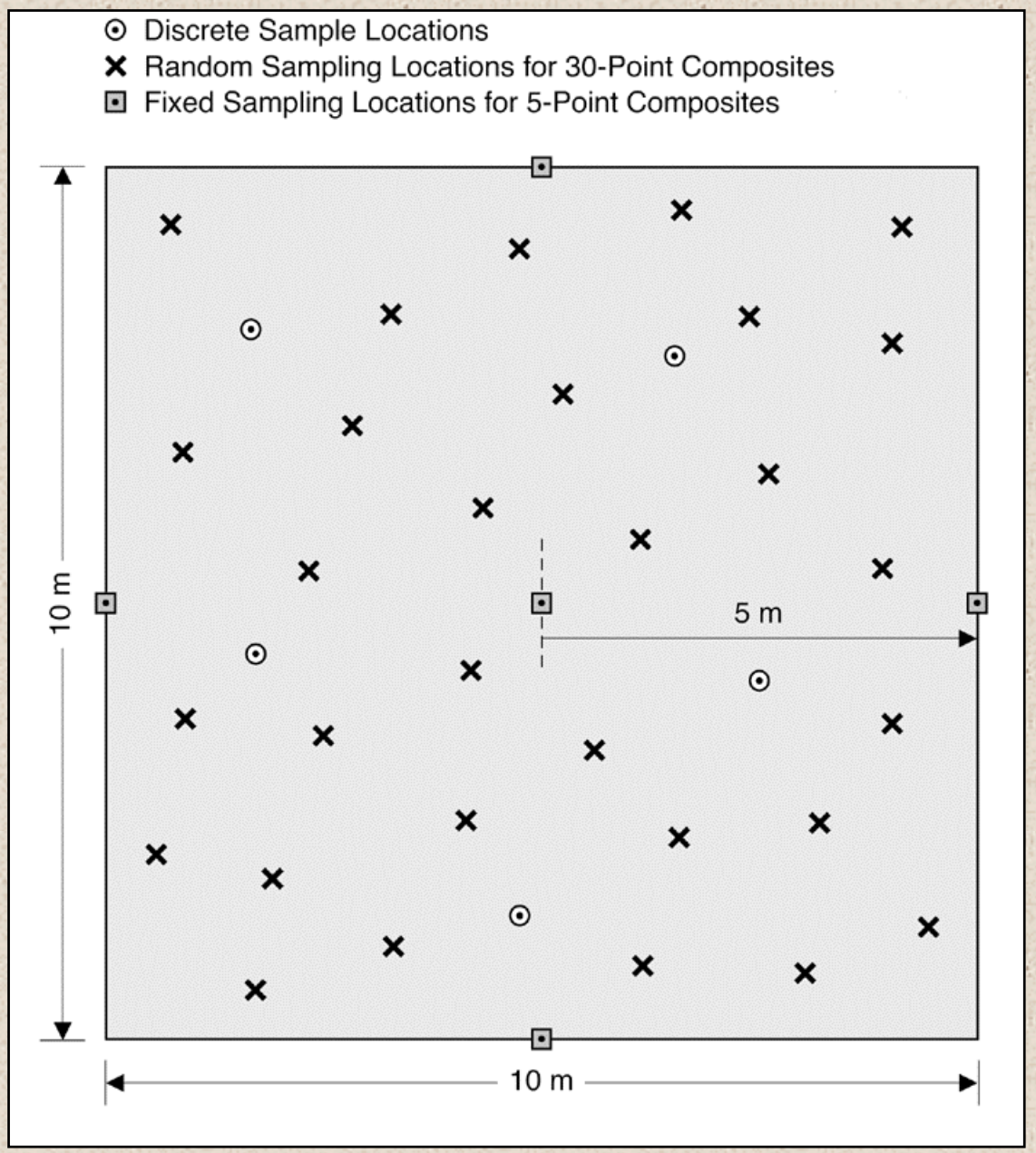
Two Low-Order
90 mm Recoilless Rifle Rounds

TNT Chunks Next to Low-Order 90 mm Round

Low-Order 2.75-in Rocket Warhead

10 x 10 m Grid at Ft. Bliss

Chunks of TNT Collected from 10 x 10 m Grid at Ft. Bliss



Ft. Bliss
10-m x 10-m Grid

Methods:

- Five discrete samples
- Seven 30-increment composite samples
- Five 5-increment composite samples

Ft. Bliss 10-m x 10-m Grid

Results:

- Five discrete samples

  <0.016, <0.016, 0.048, 0.124,0.134 µg/g

- Seven 30-increment composite samples

  0.019, 0.020, 0.083, 0.088, 2.0, 3.1 µg/g

- Five 5-increment composite samples

  <0.016, <0.016, <0.016, 0.027, 0.078 µg/g

Conclusions from Site Characterization Studies

- **Artillery and mortar ranges** – RDX and TNT in surface soils in low ppb, distribution spatially very heterogeneous, hot spots present, low-level GC-ECD method required for characterization of some areas
- **Ruptured UXO items and low-order detonations** – Localized contamination results in concentrations of main charge explosives in % range in near surface soils
- **Antitank ranges** – Major contaminant HMX, concentrations in the tens to hundreds of ppm, TNT concentrations only about 1/100 as high, HMX concentration a function of distance from target
- **Hand grenade ranges** – Major contaminants RDX and TNT, concentrations in low ppm range, distribution more homogeneous than found for other impact ranges
- **Firing points** – Major contaminants NG and 2,4-DNT, concentration in low ppm range, distribution less heterogeneous than impact areas, deposition at least as far as 75 m from muzzle

Questions?

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